EPJ Web of Conferences **132**, 03027 (2017) DOI: 10.1051/epjconf/201713203027
SPECTROSCOPY.SU 2016

Electronic structure and luminescence properties of $Ca_2Ge_7O_{16}:Dy^{3+}$

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Abstract. The present report represents an overview of the results of a combined experimental-computational study of electronic structure, thermoluminescence (TL) and afterglow properties of $Ca_2Ge_7O_{16}:Dy^{3+}$ synthesized for the first time. Afterglow curves of $Ca_2Ge_7O_{16}:Dy^{3+}$ at 575 nm showing persistent luminescence have been described in Becquerel law. The TL measurements reveal at least one TL band at 326 K and two luminescence bands at 475 and 535 nm. Persistent luminescence in $Ca_2Ge_7O_{16}:Dy^{3+}$ originates from relatively shallow charge traps with high probability of charge carriers recapture. The model of energy processes, configurations of traps and luminescence centers has been proposed with the aid of *ab initio* calculations performed using the LCAO approximation and several hybrid functionals.

Calcium and cadmium heptagermanates ($M_2Ge_7O_{16}$, M = Ca, Cd) are considered for development of multifunctional materials. The compounds have been extensively studied for their applications in anodes for lithium-ion batteries with excellent cycling performance, high capacity and superior rate capability [1]. Meanwhile, lanthanide-doped $M_2Ge_7O_{16}$ (M = Ca, Cd) demonstrate the possibility of their use as promising optical storage devices [2, 3].

The optical band gap of 5.50 eV in the $Ca_2Ge_7O_{16}$ (space group P–4b2, Z = 2) host has been evaluated from the diffuse reflection spectrum employing the Kubelka-Munk approximation. The band structure, density of states and partial density of states have been obtained from the results of DFT calculations performed using the LCAO approximation and several hybrid functionals which have shown the closest E_g^{opt} value (5.97 eV) to the experimentally estimated counterpart when the WC1LYP functional [4] has been applied.

While the highest intensity of photoluminescence in $Ca_{2-3x}Dy_{2x}Ge_7O_{16}$ in the visible spectral range is attained at x = 0.0075, $Ca_{1.985}Dy_{0.010}Ge_7O_{16}$ reveals the most pronounced orange afterglow in intensity and decay time. Persistent luminescence in $Ca_{1.985}Dy_{0.010}Ge_7O_{16}$ is observed for 60 min under 230 nm UV excitation (E^{ex} = 5.39 eV) for 5 min. Longer excitation time stimulates the detectable afterglow in $Ca_{1.985}Dy_{0.010}Ge_7O_{16}$ up to few hours.

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The energy of UV excitation of $Ca_{2-3x}Dy_{2x}Ge_7O_{16}$ (5.39 eV) is approximately equal to the value of the optical band gap (5.50 eV). The presence of defects in the structure of $Ca_{2-3x}Dy_{2x}Ge_7O_{16}$ ($0 \le x \le 0.0075$) leads to additional acceptor levels in the forbidden gap near the bottom of the conduction band. The incident UV irradiation with the energy of 5.39 eV can be assumed to excite directly the corresponding trap levels. Duration of the observed afterglow depends on the energy of traps in the band gap. The maximal energies of the relatively shallow traps (1.00 eV and 0.72 eV) have been derived from the standard fitting of the measured thermoluminescence glow curves [5].

A possible mechanism of persistent luminescence with CIE chromaticity coordinates $x = 0.529$, $y = 0.429$ has been proposed for $Ca_2Ge_7O_{16}:Dy^{3+}$ that is similar to energy migration scheme discussed in [3]. Under UV irradiation, the excited electrons from the ground level of the host are captured by the native traps generated in $Ca_2Ge_7O_{16}$. During thermal disturbance at room temperature, captured electrons can be easily released to create the blue afterglow from the host. In dysprosium-doped $Ca_2Ge_7O_{16}$, the energy from the host emission transfers to excite energy levels of Dy^{3+}. The traps introduced by doping with Dy^{3+} form a bridge between the host and Dy^{3+} that promotes persistent energy transfer from the host to Dy^{3+} after the removal of exposure source. The shallow traps can also serve as trapping centers which distribute around the 4*f* states of Dy^{3+} near the bottom of the conduction band, therefore, more captured carriers transfer to Dy^{3+} after the removal of exposure source.

This work was partially supported by the FASO Program No. 0397–2015–0020 and RFBR Grant No. 14–03–31324. Computational procedures were carried out at the URAN Computing Platform at IMM UB RAS (Ekaterinburg, Russia). I.I.L. would like to acknowledge support from the Russian President Fellowship SP–931.2016.1.

References

1. Z.L. Hu, S. Zhang, C.J. Zhang, G.L. Cui, Coord. Chem. Rev. **326**, 34 (2016)
2. S.J. Yi, Y.L. Liu, J.X. Zhang, D.S. Yuan, J.H. Rong, L.H. Huang, Chinese J. Inorg. Chem. **20**, 247 (2004)
3. T. Wang, J. Gou, X.H. Xu, D. Zhou, J.B. Qiu, X. Yu, Opt. Express **23**, 12595 (2015)
4. R. Demichelis, B. Civalleri, M. Ferrabone, R. Dovesi, Int. J. Quant. Chem. **110**, 406 (2010)
5. R. Chen, S.W.S. McKeever, *Theory of thermoluminescence and related phenomena* (World Scientific Pub. Co., Singapore, 1997)